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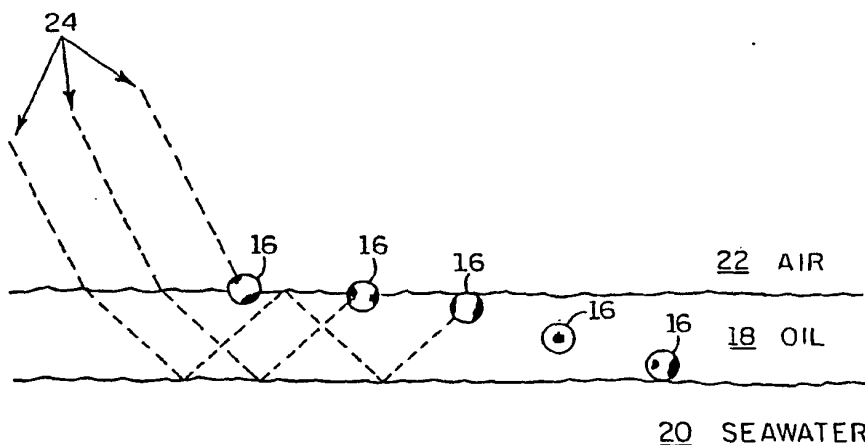
(57) Abstract

A bead (16) having an exterior surface which is at least partially coated with a material that under illumination and in the presence of air is capable of accelerating the oxidation of organic compounds floating on water. The coated bead is water floatable and has an equivalent diameter of less than about 2 mm, preferably on the order of 10-30 microns. These coated beads can be used to accelerate under illumination oxidation of a floating oil film (18) (e.g. from an oil spill) by dispersing the coated beads in the film and allowing them to be exposed to solar illumination (24) and oxygen.

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+ DESIGNATIONS OF "SU"

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— 1 —

MATERIALS AND METHODS FOR PHOTOCATALYZING
OXIDATION OF ORGANIC COMPOUNDS ON WATER

10   This invention relates to materials and methods for photocatalyzing the oxidation of organic compounds floating on water, such as those typically resulting from an oil spill.

15   Oil spills in the world's oceans and seas have a potentially damaging effect on the environment.   Oil entering the seas can have a harmful impact not only upon the marine ecosystem, but also upon commercial and recreational resources of coastal areas.

20
            Organic compounds invade the world's waterways from many sources in addition to oil spills.   For example, refineries located along rivers often introduce substantial amounts of organic products and waste into the water..
25   Organic compounds from landfills and waste sites can leach down   to   water   tables   below   the   earth's   surface. Recreational motorboats often exhaust and leak a certain amount of oil and gasoline into lakes and reservoirs. These are just a few of the sources of organic compounds
30   entering water resources.

            The problems associated with petroleum in water may be ameliorated over time through various natural treatment processes.   Among these are evaporation, dissolution,
35   dispersion, adsorption onto suspended particulate matter, sinking, and microbial oxidation.

            Another naturally occurring process for treating oil films on water is photocatalytic oxidation (alternatively

-2-

referred to as photoassisted or photochemical oxidation or as photooxidation). Since oil and related organic materials generally have a lower density than water, they tend to float on the surface of water as a film, and are

5   thereby exposed to a significant amount of solar illumination. Natural photocatalytic oxidation of floating oil films has been the subject of several studies, and it is generally known that oxidation of organic compounds in oil can be naturally photocatalyzed and that the oxidation

10   products are generally more water soluble and/or less refractory compounds, such as alcohols, ketones, and carboxylic acids. These photooxidation products may be environmentally less harmful, because after dissolving, they tend to be more readily attacked by microorganisms for

15   eventual complete oxidation to CO_2.

Techniques for cleaning oil slicks have been tried and are discussed in the literature. For example, mechanical clean-up methods, such as the use of booms, skimmers, and

20   absorbents, have been used. However, these are impractical in many situations.

Chemical techniques have also been tried. For example, dispersants and emulsifiers may be used to

25   accelerate natural dispersion of oil. However, these techniques are environmentally damaging in many situations, as they may simply direct the oil and resulting damage away from the water surface to underlying depths.

30   Another technique which has been suggested is the use of organic photosensitizers to photocatalyze the oxidation of the oil film. A potential problem with this type of technique is that the wavelengths needed to excite the oil-dissolved photosensitizer are often absorbed by other

35   constituents of the oil film. Furthermore, even if the photosensitizer has been excited by a photon, it may be "quenched", i.e. transfer energy to another dissolved

compound that is not an adequate photosensitizer. Therefore, this technique has not been widely accepted.

5   Thus, there is a continuing need for environmentally safe and beneficial methods for treating organic compounds which float on and plague the surface of bodies of water. It is an object of this invention to provide materials and methods for such treatment which overcome or reduce at least some of the disadvantages of the prior art.

10

One broad aspect of the present invention provides a bead having an exterior surface that is at least partially coated with a material that under illumination and in the presence of air is capable of assisting in (i.e.

15   accelerating) the oxidation of organic compounds floating on water, the coated bead being water floatable. The term "bead" is used broadly herein to mean a piece of material having virtually any three-dimensional shape (e.g. spherical, octahedral, prismatic, or of irregular cross-

20   section). The coated beads contemplated by this invention have an equivalent diameter of less than about 2 millimeters.

The term "equivalent diameter" is used herein to mean

25   the diameter of a sphere which would have the same volume as the bead. Thus, for example, if the bead has a volume of $pi/6$ mm^3, it has an equivalent diameter of 1 mm.

The term "water floatable" means that the coated bead

30   has such physical characteristics that it will float at or near the surface of water either indefinitely (e.g. until washed ashore or dissolved) or for a sufficient period of time such that the material coated on the bead can be effective to assist in, induce or accelerate oxidation of

35   organic compounds floating on the water under sunlight. The coated bead may be made floatable in at least three ways. First, the coated bead may have a density less than

-4-

the density of water. Second, the coated bead can be
treated such that it is substantially hydrophobic (i.e.
oleophilic), and therefore be kept by interfacial forces on
the film near the water surface. Finally, the coated bead
5   can be made sufficiently small for the sedimentation
velocity to be substantially reduced, particularly in
viscous oils. By making coated beads of such small
dimension, their precipitation time through an oil film may
be long enough such that they are in contact with the oil
10   film for a sufficient length of time to effect
photooxidation thereof. For example, the coated bead size
could be small enough such that the sedimentation velocity
would be on the order of 10^{-6} centimeters per second,
thereby making their precipitation time through a typical
15   oil film longer than about 24 hours.

Preferably, when used to treat oil slicks on the
surface of an ocean or sea, the coated beads provided by
this invention have a density less than the density of sea
20   water. The coated beads will therefore tend to float along
with the oil slick on the surface of the sea water. More
generally, the coated beads preferably have a density less
than the density of the water onto which they are to be
dispersed.
25

Preferably, the bead has a relatively high index of
refraction, and the coating material has an even higher
index of refraction. In this way, the bead may tend to
trap and waveguide light to the photocatalytic coating
30   material. This is desirable, since generally the more
light that reaches the photocatalytic coating material, the
greater the photon flux for photoassisted oxidation of the
oil by oxygen.

35   Specifically, it is preferred that the photocatalytic
coating material have an index of refraction of at least
about 2. Examples of such materials are zinc oxide

-5-

(n = about 2), zinc sulfide (n = about 2.3), titanium
dioxide (n = about 2.8), and iron oxide (n = about 2.9).
It is preferred that the bead have an index of refraction
of at least about 1.5 (as is typical of most SiO_2 - based
5   glasses) or 1.6 (as is typical of most ceramics).

The term "index of refraction" as used herein is that
measured at the sodium D-line near 589 nm. In the context
of a hollow bead as used in certain embodiments of this
10   invention, the index of refraction refers to the bead shell
material only, and not the hollow (air) interior.

The coating material preferably comprises an n-type
semiconductor having a band gap of at least about 2 eV.
15   The coating material is also preferably photoconductive.
Specific compounds which may be used alone or in
combination as the coating material include titanium
dioxide, zinc oxide, zinc sulfide, and iron oxide. Other
compounds may be effective as photocatalysts, but may be
20   less preferable either because of their toxicity, or
because of their photodecomposition (i.e. photooxidation of
their surface or photodissolution).

Preferably, the beads comprise an inorganic material,
25   which generally may be coated readily with photocatalytic
compounds. For example, hollow glass or hollow ceramic
beads may be used.

Alternatively, the bead may comprise an organic
30   material. However, since a photocatalytic coating material
may tend to photocatalyze the oxidation of an organic bead
material by oxygen, the bead preferably should be protected
with an intermediate layer comprising a material which will
not allow oxidization of the organic bead material or
35   itself be oxidized by oxygen in a process photocatalyzed by
the outer coating material. The organic bead material may
be, for example, a plastic material such as polyethylene or

-6-

polypropylene. The protective intermediate layer may be for example, silicon dioxide or aluminum oxide.

In general, the smaller the coated bead provided by this invention, the more economical it will be in use. In any event, the size of each coated bead is preferably less than the thickness of the oil film to be treated.

In order to take advantage of the optical properties of the coated beads and their ability to trap light, the lower limit on the equivalent diameter of the coated beads is on the order of about one tenth of the wavelength of light. This is so because if the beads are smaller, their dielectric properties (including their index of refraction) tend to be averaged with those of the medium in which they are immersed, and light of appropriate wavelengths (e.g. longer than 200 nm) will not be substantially refracted or reflected at the particle-liquid interface. In order to optically guide and trap light, coated beads with an equivalent diameter of at least about 30-100 nm are thus preferred.

Preferably, the coated beads provided by this invention have an equivalent diameter of less than about 200 microns, more preferably less than about 100 microns, and most preferably between about 10 and 30 microns, but have at least a 30 nm equivalent diameter.

In certain embodiments, the invention provides coated beads which are oil dispersible and water floatable and capable of accelerating the oxidation of hydrocarbons in the presence of oxygen and light. The term "oil dispersible" as used herein means that the coated beads are capable of being dispersed in or on oil. That is, they may have a surface that makes them wetted by oil.

In another broad aspect, the present invention provides a method for treating an oil film floating on a body of water using the coated beads described above. The method comprises the steps of dispersing a plurality of

5   such coated beads on an oil film, and allowing the coated beads to be exposed to solar illumination and ambient air, thereby accelerating the oxidation of organic compounds in the oil film. Preferably, the coated beads have an average equivalent diameter less than the average thickness of the

10   oil film, and the coated beads float at or near the surface of the oil film. In certain embodiments, light may be trapped by the beads and waveguided to the coating material.

15   Finally, in another broad aspect, the present invention provides a method for treating an oil film floating on a body of water comprising the steps of dispersing a plurality of water floatable particles on the oil film, the particles comprising a material that under

20   illumination and in the presence of air is capable of oxidizing organic compounds in the oil film. The particles are allowed to be exposed to solar illumination and ambient air, thereby accelerating the oxidation of organic compounds in the oil film.

25

The term "particle" is intended to mean any form of solid particulate matter, but is not intended to include individual dissolved molecules. Specifically, the term particle as used herein includes particulates having on the

30   order of at least 5 nm physical dimension.

Preferably, the particle material comprises an inorganic material, such as an n-type semiconductor having a band gap of at least about 2 eV. The particle material

35   is also preferably photoconductive. Appropriate materials for use in this method include titanium dioxide, zinc oxide, zinc sulfide, and iron oxide.

-8-

        Figure 1 is an exterior view of a partially coated
bead as provided by a preferred embodiment of the present
invention.

5   Figure 2 is a sectional view of the coated bead shown
in Figure 1.

        Figure 3 is an exterior view of another partially
coated bead as provided by this invention.

10

        Figure 4 is a schematic drawing showing coated beads
dispersed in an oil film floating on water, as provided by
preferred methods of practicing this invention.

15   Various   embodiments   of   this   invention   provide
environmentally safe technology for treating crude oil
slicks resulting from oil spills, in the form of coated
beads designed to float with and photoassist in (i.e.
photocatalyze) the oxidization of oil slicks when exposed
20 to sunlight and oxygen dissolved in oil, dissolved in
water, or in air.

        In a preferred embodiment, the beads consist of hollow
glass or ceramic microspheres of about 10-30 microns
25 diameter.   Beads of this type are manufactured and are
commercially available.   Their density is about 0.4 g/cm^3
for glass beads and about 0.7-0.8 g/cm^3 for ceramic beads.
Microbeads of 10-30 microns diameter are nearly invisible
to the human eye, and thus not an eyesore.   Larger
30 microbeads could alternatively be used and would typically
have the appearance of white sand.

        Figs. 1 and 2 illustrate a preferred coated bead 10
for use in this invention.   Each hollow bead 11 may be
35 coated at random sites with a photocatalytic coating
material 12, resulting in a bead with coated areas 13 and
uncoated areas 14.   The bead may alternatively be fully

-9-

coated, but is preferably only partially coated so as to save on coating material. In this case, sunlight may enter the coated bead 10 through exposed areas 14 and may be waveguided to the coating material 12, as described in more

5   detail below.

In an alternative embodiment as illustrated in Fig. 3, the coating material 12' may be dispersed relatively uniformly on the bead 11'.

10

In a preferred embodiment, the coating material 12 comprises TiO_2 pigment particles having diameter on the order of 30-200 nm. TiO_2 (rutile) or TiO_2 (anatase) are particularly preferred for use in this invention, as they

15   are widely used white pigments, and are well known as photocatalysts in the oxidation of contacting organic compounds.   Both   are   substantially   nontoxic   and environmentally harmless.   Both are n-type semiconductors with 3 eV and 3.3 eV band gaps, respectively.   The high

20   index of refraction (n=2.8) that makes TiO_2 (rutile) an excellent light scatterer also makes it a good collector of photons in the present system.

There is a great amount of literature on photoassisted

25   (i.e. photocatalytic) oxidations with TiO_2.   It has been theorized that absorption of a photon by TiO_2 produces an electron-hole pair.   The photogenerated holes oxidize directly contacting organic compounds.   The electrons reduce oxygen to a surface-bound peroxide, that also

30   photooxidizes organic compounds. (It should be appreciated that any proposed theory presented herein is for illustrative purposes only, and the claims and disclosure should not be construed as being bound thereto).

35   Preferably, the coated bead 10 is engineered to have a density of around 0.4-0.9 g/cm^3, and the regions 14 of the

bead that are not n-TiO$_2$ particle coated are made
hydrophobic (i.e. oleophilic). In use, such coated beads
will tend to be attracted to and float with an oil layer.

5   The coated beads may be prepared by starting with
commercial hollow glass or ceramic microspheres and
depositing on their surfaces a semiconducting photocatalyst
by a gas phase process. For example, the surface of the
beads may be prepared in a fluidizing bed arrangement by
10   flowing through a stream of dry nitrogen that contains a
surface di- or trialkoxy (or chloro) silane. Subsequently,
a gaseous dispersion of TiO$_2$ pigment particles may be passed
through the bed of activated microspheres.

15   Alternatively, the surface of the ceramic beads may be
coated by a smoke of partially hydrolized, reactive
titanium tetrachloride (TiCl$_4$) or tetraalkoxide (Ti(OR)$_4$).

Simple and inexpensive methods exist for making SiO$_2$
20   (glass) hydrophobic (i.e. oleophilic) and thus obtain an
oil-wetted coating on the bead, such as exposure to
trimethyl chlorosilane vapor (e.g. a dry air-stream with
trimethyl chlorosilane). Only one monolayer is typically
needed to make the surface hydrophobic. Thus, the
25   partially coated bead 10 may be exposed to such a material
to render it substantially hydrophobic. Although the
resulting hydrophobic organic monolayers may be
photooxidized on the bead areas 13 coated with n-TiO$_2$
particles 12, they will remain on the uncoated glass or
30   ceramic surface 14. Alternatively, the bead 11 surface may
first be made hydrophobic, and subsequently partially
coated with photocatalytic material 12.

As illustrated in Fig. 4, a plurality of water
35   floatable, partially coated beads 16 may be dispersed
within an oil film 18 on water 20. The beads 16 may be of

-11-

varying density and degree of hydrophicity, and thus reside
at differing depths of the oil film 18, as shown in Fig. 4.
The diameter of the beads 16 is preferably less than the
thickness of the oil film 18.

5

Typically, an oil film (n = about 1.45) is bounded by
two media with lower refractive index, i.e. air (n = 1.00)
and seawater (n = about 1.34). Because of this, attenuated
total reflection of incident sunlight may occur, causing

10   part of the light to propagate in the oil film. The
critical trapping angles at the air-oil and oil-water
interfaces to achieve such propagation are typically about
around 46ˆ and 72ˆ, respectively.

15   This phenomenon may be used advantageously in the
practice of this invention. Referring again to Fig. 4, the
coated beads 16, being preferably made of glass or ceramic,
have an index of refraction at some or all of their surface
of approximately 1.5 or more, which is above that of

20   seawater and oil. Thus, incident sunlight (represented as
dashed lines 24) may be partially trapped initially in the
oil film 18, and then in the higher index coated beads 16·
by total internal reflection of the light.

25   Because the index of refraction of TiO_2 (rutile) is
about 2.8 (well above the index of the glass or ceramic),
the light may be waveguided to the TiO_2 coating particles.
By analogy, the effect may be similar to a high index dust
particle (analogous to the TiO_2 on the bead) on an optical

30   fiber (analogous to the oil film) carrying a laser beam
(analogous to the reflected sunlight).

As a result, both direct and reflected light can reach
the photocatalytic coating material on the coated beads 16.

35   Photons of less than 3 eV energy, absorbed by the
particles, can produce a flux of oxidizing holes and

-12-

peroxide forming electrons, thereby accelerating oxidation of organic compounds in the oil film 18.

In typical applications, some of the trapped light may be lost by absorption in the oil. In light crudes that are nearly colorless, there may be little attenuation. Nevertheless, even in typical heavy crudes, which at 337 nm may have extinction coefficient near 20 cm^{-1}, much of the light trapped in the oil film may end up in the high refractive index TiO_2-coated microbead.

The actual solar radiation collecting area per microbead will typically depend on the extinction coefficient through the 300-400 nm range. Even for highly absorbing oils, the effective collection area per microbead may be greater than approximately 0.01 cm^2, considerably larger than the actual bead surface area of the smaller beads of this invention.

In typical cases, the initial photooxidation products will be slightly water soluble alcohols, ketones, and carboxylic acids. Though not proven to be safe to sealife, these products can be highly diluted as they can dissolve in seawater. Also, the photooxidation products may be far more rapidly attacked by microorganisms (that eventually oxidize them to CO_2) than the hydrocarbons of a slick.

In the following discussion, a conservative estimate of oil slick removal rates is presented, based only on the bead surface area, without assuming any waveguiding in the films. The average daylight solar irradiance, at all wavelengths is, in the mid-latitudes, approximately 700 W/m^2. About 1.5% of the solar flux can produce an electron-hole pair in TiO_2--that is, exceeds the 3.0 eV band-gap of this semiconductor. Thus, the useful flux is approximately 10 W/m^2. For a 3 eV semiconductor, this represents an

-13-

electron or hole current density of 3.3 A/m^3. When holes
directly oxidize the oil, and when electrons reduce O$_2$ to a
(TiO$_2$ surface-bound) oxidizing peroxide, two equivalents of
oxidizer are produced per photon absorbed. Thus, if a
5   hydrocarbon is solubilized by a two-electron oxidation
reaction (e.g. is converted to an alcohol), the solar flux
limited rate of oil stripping is about 3.2x10^{-5} moles/m^{2}sec
or approximately 1.4 moles/m^{2}day (1 day = 12 h.). If 4 or
6 electron-oxidation reactions are required to dissolve the
10   oil, the corresponding values are approximately 0.7 and 0.5
moles/m^2, respectively. 0.7 moles/m^{2}day translates for the
hydrocarbon dodecane (MW 170) to approximately 120 g/m^{2}day,
equivalent to 8x10^{-4} barrels/m^{2}day, i.e. to elimination of
an oil film of 0.1 mm thickness over the 1 m^2 area in one
15   day. Assuming that the hydrophobic particles float and
stay with the oil slick until it is destroyed, and that
their actual activity is only 0.2 of theoretical, 1 m^2 of
the microbeads will eliminate in one month 5x10^{-3} barrels of
oil. Since the diameter of the preferred beads is
20   approximately 10-30 microns, about 6 g of material will
cover 1 m^2 of area (this is a conservative estimate, since
each microbead may actually collect light from an area that
is 10-100 times its own, even in a heavy, strongly
absorbing crude, because of the waveguiding properties of
25   the oil film). At a cost of $1/lb, the materials cost is
approximately 1.3¢/m^2. The corresponding materials cost for
cleaning up 1 barrel of oil in one month is thus less than
$2.60.

30   In an ocean clean-up, coated microbeads provided by
this invention may be carried in and dispersed from bulk
grain or fertilizer carrying ships, then dispersed on the
ocean surface with the oil, by wind and waves. Because the
coated beads are preferably hydrophobic and because their
35   density can be adjusted to be somewhat less than that of
crude oil, they can follow the slicks, floating near their

-14-

surface. Their transportation and dispersion costs should be similar to those for bulk free-flowing fertilizers.

It should be appreciated that in the preferred embodiments described above, the materials used for the beads and bead coatings are substantially safe to ingest, and thus will not significantly harm humans, fish, birds or vegetation.

EXAMPLE

The following example is designed to illustrate certain aspects of the present invention. The example is not intended to be comprehensive of all features and all embodiments of the present invention, and should not be construed as limiting the claims presented herein.

Experiments were carried out relating to photocatalytic oxidation of films of dodecane and hexadecane on distilled water by oxygen. Quartz boats were used with a free liquid surface area in the boats of ca. 20 cm^2. A filtered medium pressure Hg light source with wavelengths shorter than ca. 2900 angstroms was used for illumination. The irradiance was estimated to be around 8 mW/cm^2 on the liquid surface. The photocatalyst was n-TiO$_2$ (from Dagusa, FRG, No. P25) in the form of ca. 30 nm diameter particles.

Experiments were conducted by placing in each boat ca. 50 cc. distilled water and ca. 0.5-1 cc. of oil to form the oil films. Usually, 10-100 mg of n-TiO$_2$ particles were scattered on the surface of the oil film prior to irradiation. The boats with water, oil and photocatalyst were placed under the UV light source and allowed to remain for periods from 12-72 hours. Residual oil remaining was determined by pouring the contents of each boat into a

-15-

burette.   This procedure had been determined to yield
adequate accuracy in a number of tests on known oil
volumes.

5   In one series of runs using hexadecane as the oil,
illumination by the UV light source of a first boat with
water, hexadecane oil films and n-TiO$_2$ photocatalyst was
carried out for ca. 65 hours.   A second boat containing
identical amounts of water, hexadecane but no n-TiO$_2$ was
10   also exposed to the UV illumination.   A third boat
containing water, hexadecane, and n-TiO$_2$ photocatalyst was
prepared to the same amounts as in the first boat, but not
exposed to UV illumination.   The first boat was illuminated
for ca. 65 hours and was then removed from illumination.
15   The pH of the water phase was determined to be ca. 4.1.
The pH of water in the second and third boats was ca. 7.0,
characteristic of distilled water used in the experiments.
The oil phase from the three boats was subjected to GC-MS
(gas   chromatographic-mass   spectrometry)   using   chemi-
20   ionization.   The analysis showed that the first boat
yielded an oil with a composition of: $C_{10}H_{16}O_4$, $C_{12}H_{24}O$, $C_{13}H_{28}$,
$C_{13}H_{28}$, $C_{16}H_{34}$, $C_{18}H_{32}O_2$,   plus   other   undetermined   species.
(Results are somewhat uncertain as chemi-ionization was
used in MS, but library was for eii).   This together with
25   the pH reading of 4.1 shows that the n-TiO$_2$ photocatalyst
was effective in oxidizing the oil film in the presence of
UV light.

                                * * *

30   This invention has been disclosed in connection with
specific embodiments.   However, it will be apparent to
those skilled in the art that variations from the
illustrated embodiments may be undertaken without departing
the spirit and scope of the invention.

CLAIMS:

1.   A bead having an exterior surface which is at least
partially coated with a material that under illumination
and in the presence of air is capable of accelerating the
oxidation of organic compounds floating on water, the
coated bead being water floatable and having an equivalent
diameter of less than about 2 mm.

2.   The coated bead of claim 1 which has a density less
than the density of sea water.

3.   The coated bead of claim 1 which has a density less
than the density of water.

4.   The coated bead of claim 1 which has a density less
than 0.9 g/cm^3 at 20°C.

5.   The coated bead of claim 1 which has a density less
than 0.7 g/cm^3 at 20°C.

6.   The coated bead of claim 1 which is substantially
hydrophobic.

7.   The coated bead of claim 1, wherein the bead is
additionally coated with a substantially hydrophobic
material.

8.   The coated bead of claim 1, wherein the bead has an
index of refraction of at least about 1.5.

-17-

9.   The coated bead of claim 1, wherein the bead has an index of refraction of at least about 1.6.

5   10.   The coated bead of claim 1, wherein the coating material has an index of refraction of at least about 2.0.

11.   The coated bead of claim 1, wherein the index of
10   refraction of the coating material is higher than that of the bead.

12.   The coated bead of claim 1, wherein the coating
15   material comprises an n-type semiconductor having a band gap of at least about 2 eV.

13.   The coated bead of claim 1, wherein the coating
20   material comprises a photoconductive material.

14.   The coated bead of claim 1, wherein the coating material comprises titanium dioxide.
25

15.   The coated bead of claim 1, wherein the coating material comprises zinc oxide, zinc sulfide, or iron oxide.

30
16.   The coated bead of claim 1, wherein the bead comprises a glass material.

35   17.   The coated bead of claim 1, wherein the bead comprises a ceramic material.

-18-

18. The coated bead of claim 1, wherein the bead comprises a plastic material coated with an intermediate layer comprising a material which will not accelerate the oxidation of the plastic material by air or be itself oxidized under illumination and in the presence of air by the outer coating material.

19. The coated bead of claim 18, wherein the plastic material comprises polyethylene or polypropylene.

20. The coated bead of claim 18 or 19, wherein the intermediate layer material comprises silicon dioxide or aluminum oxide.

21. The coated bead of claim 1 which has an equivalent diameter of less than about 200 microns.

22. The coated bead of claim 1 which has an equivalent diameter of less than about 100 microns.

23. The coated bead of claim 1 which has an equivalent diameter of between about 10 and 30 microns.

24. The coated bead of claim 1 which has an equivalent diameter of at least about 30 nm.

25. A coated bead which is oil dispersible and water floatable and capable of accelerating the oxidation of hydrocarbons in the presence of oxygen and light.

26. A method for treating an oil film floating on a body of water, comprising the steps of:

dispersing a plurality of water floatable particles on
such an oil film, the particles comprising a
material that under illumination and in the
presence of air is capable of accelerating the
oxidation of organic compounds in the oil film;
and

allowing the particles to be exposed to solar
illumination and ambient air.

27. The method of claim 26, wherein the particle material comprises an inorganic material.

28. The method of claim 26, wherein the particle material comprises an n-type semiconductor having a band gap of at least about 2 eV.

29. The method of claim 26, wherein the particle material comprises a photoconductive material.

30. The method of claim 26, wherein the particle material comprises titanium dioxide, zinc oxide, zinc sulfide, or iron oxide.

31. A method for treating an oil film floating on a body of water, comprising the steps of:

dispersing a plurality of beads on such an oil film,
the beads being at least partially coated with a

-20-

material that under illumination and in the
presence of air is capable of accelerating the
oxidation of organic compounds in the oil film,
each coated bead being water floatable and having
an equivalent diameter of less than about 2 mm;
and

allowing the coated beads to be exposed to solar
illumination and ambient air.

32. The method of claim 31, wherein each coated bead has
a density less than the density of sea water.

33. The method of claim 31, wherein each coated bead has
a density less than the density of water.

34. The method of claim 31, wherein each coated bead has
a density less than 0.9 g/cm^3 at 20°C.

35. The method of claim 31, wherein each coated bead has
a density less than 0.7 g/cm^3 at 20°C.

36. The method of claim 31, wherein the coated beads float
at or near the surface of the oil film.

37. The method of claim 31, wherein each coated bead is
substantially hydrophobic.

-21-

38. The method of claim 31, wherein each bead is additionally coated with a substantially hydrophobic material.

5

39. The method of claim 31, wherein each bead has an index of refraction of at least about 1.5.

10   40. The method of claim 31, wherein each bead has an index of refraction of at least about 1.6.

15   41. The method of claim 31, wherein the coating material on each bead has an index of refraction of at least about 2.0.

20   42. The method of claim 31, wherein the index of refraction of the coating material is higher than that of each bead.

25   43. The method of claim 31, wherein the coating material on each bead comprises an n-type semiconductor having a band gap of at least about 2 eV.

30   44. The method of claim 31, wherein the coating material on each bead comprises a photoconductive material.

45. The method of claim 31, wherein the coating material on each bead comprises titanium dioxide.

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46. The method of claim 31, wherein the coating material on each bead comprises zinc oxide, zinc sulfide, or iron oxide.

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47. The method of claim 31, wherein the beads comprise a glass material.

10   48. The method of claim 31, wherein the beads comprise a ceramic material.

49. The method of claim 31, wherein each bead comprises a
15   plastic material coated with an intermediate layer comprising a material which will not accelerate the oxidation of the plastic material by air or itself be oxidized by the outer coating material.

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50. The method of claim 31, wherein the plastic material comprises polyethylene or polypropylene.

25   51. The method of claim 49 or 50, wherein the intermediate layer material comprises silicon dioxide or aluminum oxide.

52. The method of claim 31, wherein each coated bead has
30   an equivalent diameter of less than about 200 microns.

53. The method of claim 31, wherein each coated bead has an equivalent diameter of less than about 100 microns.

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54. The method of claim 31, wherein each coated bead has
an equivalent diameter of between about 10 and 30 microns.

5   55. The method of claim 31, wherein each coated bead has
an equivalent diameter of at least 30 nm.

56. The method of claim 31, wherein each coated bead has
10   an equivalent diameter less than the average thickness of
the oil film.

57. The method of claim 31, wherein light is trapped by
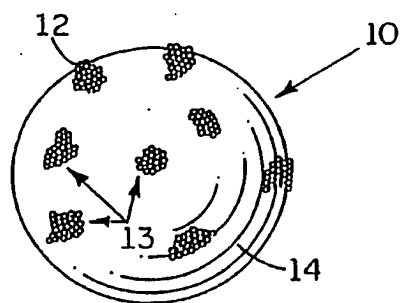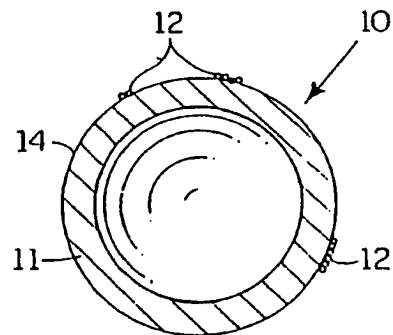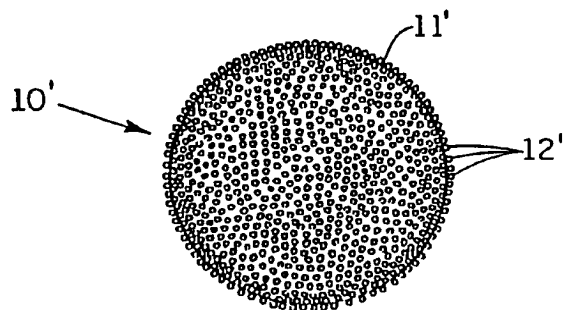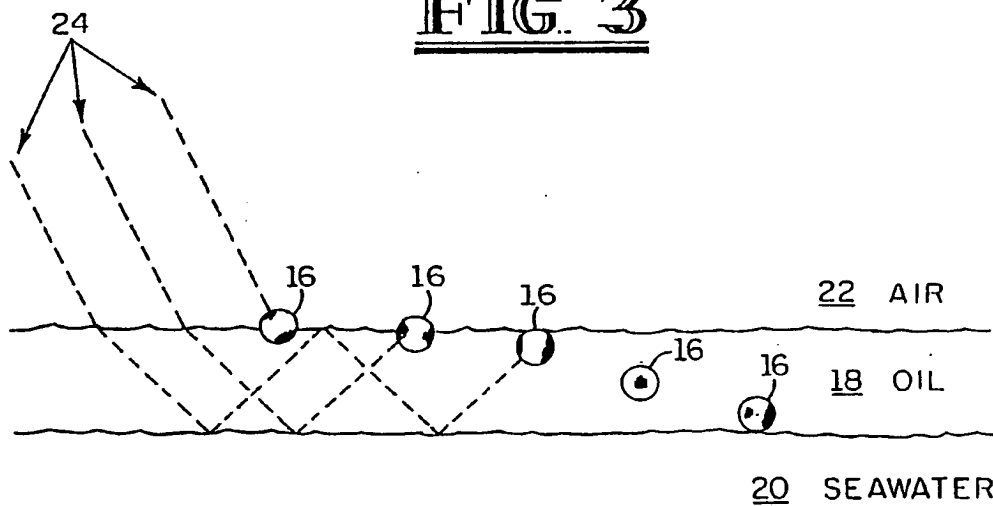15   the beads and waveguided to the coating material.

1/1

FIG. 1

FIG. 2

FIG. 3

FIG. 4

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 09 K 3/32, C 02 F 1/32, C 02 F 1/68

II. FIELDS SEARCHED

Minimum Documentation Searched [7]	
Classification System	Classification Symbols
IPC^5	C 09 K, C 02 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with Indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	DE, A, 3825905 (G. MARX) 1 February 1990, see claims 1,8,9,11; column 2, lines 49-52	1,12-15,17, 25-31,43-46, 48
A	US, A, 4806514 (C.H. LANGFORD et al.) 21 February 1989	
A	EP, A, 0234875 (NOMURA MICRO SCIENCE CO.) 2 September 1987	
A	EP, A, 0196334 (K.K. ADVANCE KAIHATSU KENKYUJO) 8 October 1986	

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* Special categories of cited documents: [10]

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29th July 1991	1 2 SEP 1991
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Mm N. KUIPER

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9006809

SA   46110

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/08/91
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		WO-A-	8601691	27-03-86
		US-A-	4788038	29-11-88